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本科毕业论文

Synthesis and characterization of hierarchically mesoporous silica nanoparticles templated by polymer-surfactant complexes

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Synthesis and characterization of hierarchically mesoporous silica nanoparticles templated by polymer-surfactant complexes

聚电解质-表面活性剂复合物为模板的多级孔结构二氧化硅纳米粒子的合成与表征

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Content

Abstract

Hierarchically porous structured materials have potential applications in catalysis, biology, biomedical and other fields, because of their variety advantages, such as high surface and pore volume, excellent permeability storage performance etc. Therefore, it has always been one of the hot spots in scientific research. In the past decades, a variety of hierarchically porous materials have been prepared, however, there are a lot of problems that have not be solved, such as hardly control of the well-defined morphology and well-ordered mesostructured as the particle size becomes smaller, complicated synthesis method and so on. So, it is meaningful to develop a simple and effective method for synthesis of hierarchically porous materials. Mesoporous silica nanoparticles have unique advantages in the areas of catalysis, adsorption, separation, biosensing, and biological sciences due to their dual function of porous materials and nanoparticle materials. However, the preparation of uniform, monodisperse, size-controllable mesoporous silica nanoparticles is still a difficult problem.

Surfactants or polymers have been widely used as templates for the formation of porous materials. According to the types of polyelectrolyte, surfactant and the condition of assembly, the complex of polyelectrolyte and surfactant can have abundant ordered mesostructures. So it has a wide range of applications in the synthesis of hierarchically porous structured materials. In this thesis, a series of hierarchical mesoporous silica nanoparticles were prepared using a complex system of polyelectrolyte and surfactant. We also studied the effects of different length of surfactant complexes and different silicon precursor on the morphology and structure of the hierarchically porous materials, and highly ordered HMS nanoparticles with 2D hexagonal structure (p6mm) were firstly obtained in polymer-surfactant synthetic system. Finally apply it to the adsorption experiment to explore the rate of adsorption of mesoporous materials with different structures.

Key words： Mesoporous silica; hierarchical porous materials; mesoporous silica nanoparticles; kinetic self-assembly; polymer-surfactant complexes; mesostructure; adsorption experiment.

摘 要

介孔材料是指孔径介于 2-50 nm 的一类多孔材料。由于其较的高比表面积、规则有序的介孔孔道、孔径分布连续可调等特点，在吸附、分离、催化、电极材料、光电器件、化学传感器、非线性光学材料等领域有重要的应用价值。

多级孔结构材料由于其具有高比表面积和较大的孔体积、优异的通透性能和吸附性能等诸多优点，在催化、生物医药等领域具有重要的应用价值，因而一直是科学研究热点之一。近年来，多级孔结构材料的制备和研究已经得得到了突破性进展，各种样各的多级孔结构材料被不断地合成出来，但是在多级孔结构材料的合成与研究中仍然存在很多未能解决的问题，如其形貌和相态结构难以控制，有序结构随着粒子的变小转变为无序结构，复杂的合成方法等。因此，寻求一类简单、易操作表面活性剂或聚合物作为模板来制备多级孔结构材料，并研究其合成机制仍然具有重要的意义。介孔二氧化硅纳米粒子由于具有介孔材料和纳米粒子材料的双重功能，所以在催化，吸附，分离，生物传感和生物科学领域具有独特的优势。但是制备粒径均一的，单分散的，尺寸可控的介孔二氧化硅纳米粒子仍然是一难点。

聚电解质-表面活性剂作为模板已广泛应用于多孔材料的合成。聚电解质和表面活性剂的复合物是具有有序液晶相的介晶化合物。根据聚电解质的类型，表面活性剂和组装条件，聚电解质与表面活性剂的复合物可以具有丰富的有序介观结构，所以它在合成多级孔材料有着广泛的应用前景。在本论文中，使用聚电解质与表面活性剂的复合物体系制备了一系列多级孔介孔二氧化硅纳米粒子，并且研究了不同长度烷基链的表面活性剂和不同硅前驱体对多级孔材料的形貌和结构的影响，并首次在聚合物-表面活性剂合成体系中首次得到了具有二维六方结构(P6mm)的高度有序介孔二氧化硅纳米粒子。最后将其应用于吸附实验，探究不同结构介孔材料对丁基罗丹明吸附速率的快慢。

关键词：介孔二氧化硅　多级孔材料　介孔二氧化硅纳米粒子　动态自组装　聚电解质-表面活性剂复合物　介观结构　吸附实验

Chapter 1 Introduction

1.1 Mesoporous materials

1.1.1 Mesoporous silica material

Mesoporous materials are a type of porous materials with ordered pores on the range of 2-50 nanometers. Mesoporous materials are classified into disordered mesoporous materials and ordered mesoporous materials according to their pore structure. The former has a wide pore size distribution, and the pores have complex and irregular pore shapes and are not interconnected, the preparation is relatively simple (ordinary silica aerogels, glass-ceramics, etc.). According to classification of chemical composition, mesoporous materials can be generally divided into two major categories: silicon and non-silicon. Since the synthesis of M41S material in 1992, mesoporous silica material as a new material, with its unique characteristics, quickly attracted the attention of all scholars[1,2]. Mesoporous silica materials have many advantages, such as large specific surface area and pore volume, the size can be adjusted and distributed to teach narrow pores, controlled uniform morphology, these unique structures make it in chemical catalysis, adsorption and separation[3], biological and medicine[4], functional materials and other fields[5] to show a good application prospects.

1.1.2 The synthesis method and mechanism of mesoporous silica

Synthesis methods of mesoporous silica are usually sol-gel method, hydrothermal method, microwave synthesis and supramolecular template method. At present, the most important synthesis method is the supramolecular template method. By controlling synthesis conditions, such as temperature, concentration, pH, etc. inorganic species and organic species (supramolecular templates) combined to form mesoporous silica. The formation of mesoporous silica is mainly divided into two stages: the first stage is the formation of organic/inorganic liquid crystal phases (mesostructures), and the polymerizable inorganic precursor self-assembled under certain synthesis conditions to form an organic/inorganic composite with a mesostructure; in the second stage, the organic templating agent is removed by means of calcining or solvent extraction, The remaining space constitutes a mesoporous channel to obtain a mesoporous silica material. In the synthesis process, there are mainly four components involved in the interaction, they are supramolecular template agents, inorganic species, solvents and solution ions respectively. Among them, the template agent plays a central role in the synthesis of the entire mesoporous material. At present, commonly used

templating agents are mainly surfactants or polymers with amphiphilic properties, which can be classified into cationic, nonionic and anionic surfactants by dividing the positive and negative charges.

1.1.3 The mesostructure of mesoporous silica

Since the birth of mesoporous materials, the synthesis and characterization of mesostructures has been a key issue for mesoporous materials. Mesoporous materials are divided according to the spatial structure of the channel. So far, typical spatial structures with high order structures have been discovered: two-dimensional hexagonal (MCM-41, SBA-15), and three-dimensional cubic continuous channel (MCM-48, FDU-5), layered structure (MCM-50), three-dimensional cubic cage holes (SBA-1, SBA-11), three-dimensional hexagonal (SBA-2) and so on. Recently, hierarchically mesoporous materials (HMSs) and mesoporous silica nanoparticles (MSNs) with well-defined morphologies have received much interests due to the better adsorption and diffusion quality caused by the increase of pore channel and unique mesostructure [6-9].

1.2 Hierarchical porous materials

1.2.1 Overview of hierarchical materials

In general, hierarchical porous materials refer to a porous material having two or more different grades of pore structure, or a homogenous pore material having two different sizes. Materials with a single microporous, mesoporous, or macroporous cell structure have different advantages in their applications, but at the same time they also show some limitations, such as poor thermal and hydrothermal stability caused by the amorphous hole-wall. In order to overcome the limitation of single pore and combine the advantages of various pores, we need to synthesize a composite pore structure material to satisfy the needs of production and life. In the past decades, scientists have developed materials with hierarchical porous structures, such as hierarchical porous molecular sieves, hierarchical porous silica, and hierarchical porous carbons and so on. These materials are not only maintain the advantages of various channels, but also greatly increase the absorption and transport of macromolecular materials by hierarchical structures, as well as increase the life of the catalyst, increase the efficiency of catalytic reactions and greatly increase the economic efficiency of enterprises. Compared with single-hole materials, it shows greater application prospects in biocatalysts, petrochemicals, adsorption and separation.

1.2.2 Biomineralization and synthesis of hierarchical silica

We all know that biomineralization in nature is a very peculiar phenomenon. The process of mineralization is controlled by the organic matter secreted by the organism. Therefore, this wonderful material "manufacturing technique" in nature can inspire preparation of complex morphology of single crystal materials. Based on the mechanism of biomineralization, the continuous secretion and transport of organic matter creates the formation of hierarchical structures. The dynamic process in time has an important influence on the formation of complex topography and hierarchical structures. Diffusion of the involved substances will produce concentration gradients, in this way, different areas will have different growth and deposition rates, resulting in complex monopolies and hierarchical structures. Therefore, imitating the dynamic process of mineralization in living organisms, complex morphology and hierarchical structures can be prepared. The synthesis of mesoporous silica with hierarchical structure not only has important significance for practical application, but also has some correlation with biomineralization and biomimetic chemistry. Therefore, it has been a hot topic in the synthesis of materials[10]. The synthesis of mesoporous materials with hierarchical structures requires simultaneous control of the mesostructure and micro-scale morphology parameters at the nanoscale, as we know, the orderly mesostructure of the particles was hard to control due to the reduction in particle size. Therefore, the synthesis of mesoporous materials with hierarchical structure is still a challenging research topic in material synthesis.

1.3 Mesoporous silica nanoparticles

With the development of nano-biotechnology, intelligent organic-inorganic composite nanoparticles have attracted widespread attention. Nano-materials have shown great advantages in many fields such as biomarkers, clinical detection and treatment of major diseases. Among all nano-materials, mesoporous silica nanoparticles (MSNs) represent a class of extremely important nano-materials. In the past decades of scientific research and practical applications, significant progress has been made. MSNs materials have the advantages of good biocompatibility, large specific surface area and pore volume, tunable pore distribution, and easy surface modification of organic groups, which are very suitable as carriers for antitumor drug molecules, and are beneficial to improve the efficacy of drugs and reduce toxic side effects of drugs[11]. People can make the drug molecules exist in nano-sized small particles or amorphous state through various drug-loading methods, thereby improving the solubility or dissolution of the

drug. Although the synthesis of MSN with various morphologies and particle sizes has been reported, the synthesis of mono-disperse mesoporous silica with the size of 200 nm is still challenging. Rankin prepared hollow silica spheres with ordered mesoporous shells using cetyltrimethylammonium bromide (CTAB) and PS spheres as dual templates in concentrated aqueous ammonia media[12]. However, all these approaches generally obtained hollow spheres with smooth mesoporous silica shell layer. Sadasivan reported the synthesis of hollow microspheres with MCM-41 nanoparticles shell by alternatively deposit preformed MCM-41 particles and polyelectrolytes onto polystyrene microspheres[13,14], but it was a time-consuming procedure and multilayer of nanoparticles was needed to obtain stable hollow spheres. In the polyelectrolyte-surfactant system, few people has synthesized mesoporous silica nanoparticles with good dispersity, uniformity and highly ordered pores by a simple method.

1.4 polymer-surfactant complexes

1.4.1 The interaction between surfactants and polyelectrolyte

The quaternary cationic surfactant C_nH_{2n+1} N $(CH_3)_3Br$ (n = 8-22) is usually the most effective template for the synthesis of ordered mesoporous silica materials. The most common commercial cationic surface activity is cetyltrimethylammonium bromide (CTAB). Jimitsch surfactants, bola surfactants, polybasic surfactants, and recently reported cationic fluorinated surfaces can all be used as templates to synthesize a variety of mesostructures[15-18]. Polyelectrolytes and surfactants can form mesostructured complexes in aqueous solution. Such complexes have different phase states, such as solution and gel solids, so it has a wide range of applications in the preparation of novel nanomaterial. In 1994, Antonietti et al precipitated polymer-surfactant complexes from aqueous solutions[19,20]. They found that this complex has unique properties which were different from liquids and solids. It has the dual nature of solid and liquid. According to the SAXS test, this solid material has an order mesostructure. Ionic self-assembly of polyelectrolyte and oppositely charged surfactants can form highly ordered mesomorphous liquid crystalline phases and is a versatile tool to create supramolecular materials. A schematic diagram of the interaction between anionic polyelectrolytes and cationic surfactant molecules is shown in Fig. 1[21]. The method of using complex meso-crystalline as template will have potential application for the preparation of other ordered mesoporous porous materials.

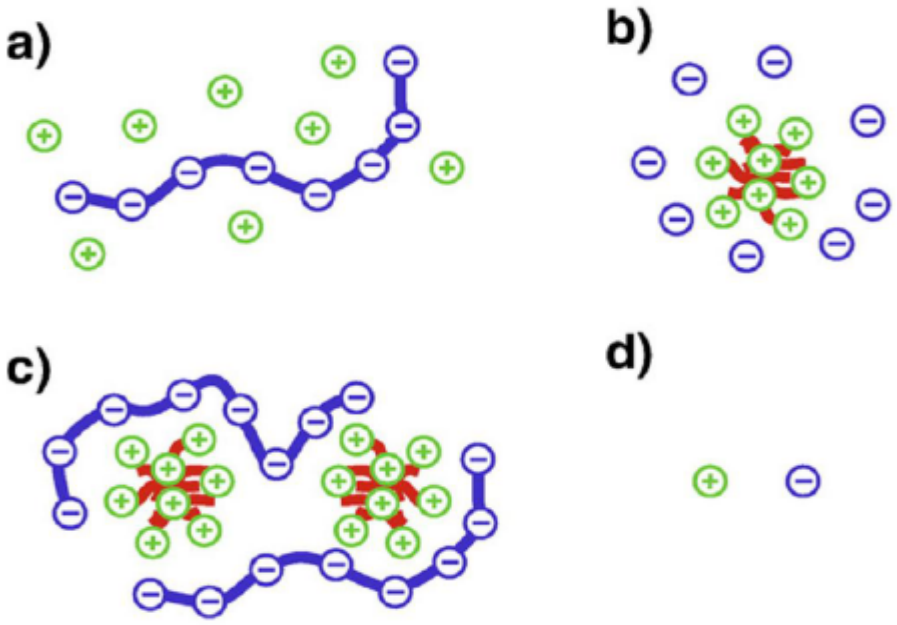

Figure 1. Illustration of the interaction cationic surfactant molecules with anionic polyelectrolyte.

1.4.2 The dynamic template of polyelectrolyte/surfactant

Although many studies have been conducted on the preparation and properties of organic complexes, the synthesis of mesoporous materials as an organic template has rarely been reported. Yang[22] et al reported the preparation of mesoporous silica films using polyethyleneimine and cationic surfactant complexes. In some other studies using mesoporous silica as a template for the preparation of mesoporous silica, an anionic polymer was introduced into the synthesis system. But in these reports, or the synthesis system was controlled under acidic conditions to avoid the anionic polymer complexes are formed with cationic surfactants[23,24], or homogeneous solutions of polymer-surfactants are obtained in mixed solvent systems[25], or the use of polymers is merely to adjust the alignment of surfactant micelles [23].

In summary, whether the anionic polymer/cationic surfactant forms the complex mesophase has not been clearly identified. In 2010, Wang[26] et al clarified the dynamic template control mechanism of polymer/surfactant complexes in the formation of hollow carved single-crystal mesoporous silica. Compared with ordinary static templates, the assembly of PAA-CTA composite template not only guides the mesoordered structure of the inorganic component with the silicon source during the assembly process, but also assembles the inorganic component and the organic phase.

The dissociation in the crystal template separates from the formation of the silicon source-micelle composite structure, that is to say, during the entire assembly process, the kinetics of the assembly process of the inorganic silicon source with the surfactant and the kinetics of the phase separation of the PAA act synergistically, so that the long-range ordering structure of the mesomorphic PAA-CTA particles is preserved in the initial state, and through the introduction of inorganic components, the mesostructure changed into pm3n mesostructures. Simultaneously, the phase separation of the polymer occurs to form a PAA domain as a template for secondary nanopores in single crystal particles.

1.5 Application of polyelectrolyte-surfactant

PAA-CTA system shows a wide application prospect in the synthesis of hierarchically porous materials and mesoporous silica nanoparticles. In previous studies, Pantazis[23] et al synthesized ordered mesoporous silica by using the mesomorphous complex of poly (acrylic acid) (PAA) and cetyltrimethylammonium bromide (CTAB) as surfactant under acidic conditions. Pang[27] et al. discussed the effect of polymers on the synthesis of mesoporous silica using cetyltrimethylammonium bromide as a template, because the relative molecular mass of the polymer was too small, no formation of the polyelectrolyte-surfactant complex was observed. Wang[26] et al have reported the synthesis of hollow carved single-crystal mesoporous silica spheres, using the mesomorphous complex of poly (acrylic acid) (PAA) and cetyltrimethylammonium bromide (CTAB) as dynamic templates under alkaline conditions. And Li[28] et al also have synthesized hierarchically nanoporous silica SBA-1 with well-defined morphology by anionic polymer PAA and cationic surfactant hexadecylpyridinium chloride (CPC) mesomorphous complexes as templates. Hierarchically structured single-crystal mesoporous silica SBA-1 nanoparticles (HMSNs) were synthesized by using a cationic surfactant and anionic polymer poly (acrylic acid) (PAA) mesomorphous complexes as a template[29]. However, we have not systematically studied the effects of different length of surfactant complexes and different silicon precursor on the morphology and structure of the materials. Below, we decided to study the effects by using surfactant complexes of different alkyl chain lengths and silicon precursors, and explore the adsorption performance of mesoporous silica materials with different structures.

Chapter 2 Experimental chemicals and instruments

2.1 Experimental chemicals

Reagent	Purity	Manufacturer
Dodecyltrimethy-lammonium bromide (C_{12}TAB)	99 %	Shanghai Macklin Biochemical Co., Ltd.
Tetradecyltrimethy-lammonium (C_{14}TAB)	99 %	Shanghai Macklin Biochemical Co., Ltd.
Cetyltrimethy-lammonium bromide (C_{16}TAB)	99 %	Aladdin Shanghai Biological Technolomagy Co., Ltd.
Octadecyltrimethylammonium bromide (C_{18}TAB)	99 %	Shanghai Macklin Biochemical Co., Ltd.
Tetraethylorthosilicate (TEOS)	SiO_2>28.0 %	Tianjin Damao chemical Co., Ltd.
Tetrapropylothosilicate (TPOS)	97 %	Shanghai Macklin Biochemical Co., Ltd.
Poly acrylic acid (PAA)	35 wt.% MW=250,000	Sigma Aldrich Chemical Co., Ltd.
Ammonium hydroxide	25-28 wt.%	Laiyang Kangde Chemical Co., Ltd.
Butyl rhodamine B	AR	Sinopharm Chemical Reagent Co., Ltd.

2.2 Experimental instruments

Instrument	Specification	Manufacturer
Electric magnetic stirrer	78-1	Changzhou Boyuan Instrument Plant
Electronic balance	BT25S	Beiting Saiduolisi Instrument Co., Ltd.
Constant temperature drying oven	SX_2-2.5-10A	Shaoxing Shangyu Daoxu Analysis Instrument Factory

Supercentrifuge	GL-20G-II	Shanghai Anting Scientific Instrument Factory
Muffle furnace	FX-202-0	Shanghai Shuli Instrument Factory
Ultrasonic machine	JP-009	Skymen Cleaning Equipment Shenzhen Co., Ltd.
PH meter	PHS-3C	Hangzhou magnetic analysis instrument factory

2.3 Test instruments

Transmission electron microscope (TEM) observations were performed on a JEOL JEM-2100 TEM microscope, working at 100 kV, it was used to study the surface morphology of the materials, the sample powder is dissolved in anhydrous ethanol, then the sample was prepared by ultrasonic dispersion of the sample, which was then added dropwise to a copper grid and dried for observation;

X-ray diffraction (XRD) measurements were performed on a Bruker Powder D8 Advance diffractometer at 40 kV and 40 mA using CuKα radiation (λ=1.5418 Angstrom), step width 0.02º, according to the position of the diffraction peak, the composite structure is judged;

Nitrogen adsorption and desorption isotherms were measured on a Tristar II 3020 sorption analyzer at 77 K. Specific surface area was calculated by BET (Brunauer-Emmett-Teller) method, the pore-size distribution was calculated from the adsorption branch using BJH (Barett-Joyner-Halenda) method and total pore volume was obtained at p/p0 of 0.99, The sample pretreatment was purged with nitrogen at 200 °C for 3 hours and then adsorbed in liquid nitrogen at a temperature of 77 K;

Dynamic Light Scattering (DLS) were performed on Mastersizer A1 POL, which can be used to observe particle size distribution, the sample powder were dissolved in water, the particle size distribution is represented by the intensity distribution of the particle size distribution;

UV-vis Spectrophotometer were performed on a cuvette containing solution, scanning wavelength range is 200-800 nm, absorption of Butyl rhodamine by the mesoporous material is measured by absorption and reflection of the liquid in the ultraviolet visible region.

Chapter 3 Experimental procedures

3.1 The synthesis of hierarchically mesoporous silica nanoparticles

In a typical synthesis, 0.55 g CTAB was completely dissolved in 25.0 ml of deionized water under stirring, and 2.0 g PAA (35 wt. % solution) was added under vigorous stirring at room temperature to obtain a clear solution. Next, 2.0 g ammonia (25%) was added to the above solution under vigorous stirring and the pH was 10-11. Immediately the solution became a milky suspension due to the formation of PAA/C_{16}TA complexes. After further stirring for 20 min, 2.08 g tetraethylsiloxane (TEOS) was added to the above solution. After being stirred for 15 min, the mixture was transferred into an autoclave, which was left at 80 ^{o}C for 48 h. The white final product was centrifuged, washed with deionized water, and dried at 80 ^{o}C. The organic templates were removed by calcination at 550 ^{o}C for 5 h.

If other synthesis conditions do not change, only the type of surfactant and the type of silicon precursors changed. The mesoporous silica were synthesized by the same number of moles of deodecyltrimethylammonium bromide (C_{12}TAB), tetradecyltrimethylammonium bromide (C_{14}TAB), cetyltrimethylammonium bromide (C_{16}TAB) and octadecyltrimethylammonium bromide (C_{18}TAB) as dynamic templates with the same number of moles of tetraethylsiloxane (TEOS) and tetrapropylothosilicate (TPOS) as silicon precursors respectively, namely, MS-C12-TE, MS-C14-TE, MS-C16-TE, MS-C18-TE; MS-C12-TP, MS-C14-TP MS-C16-TP, MS-C18-TP.

Table 1. Reactant usage information for calcined samples.

MS-C12-TE	C_{12}TAB	PAA	$NH_3 \cdot H_2O$	TEOS
	0.47 g	2.0 g	2.2 ml	2.08 g
MS-C14-TE	C_{14}TAB	PAA	$NH_3 \cdot H_2O$	TEOS
	0.51 g	2.0 g	2.2 ml	2.08 g
MS-C16-TE	C_{16}TAB	PAA	$NH_3 \cdot H_2O$	TEOS
	0.55 g	2.0 g	2.2 ml	2.08 g
MS-C18-TE	C_{18}TAB	PAA	$NH_3 \cdot H_2O$	TEOS
	0.59 g	2.0 g	2.2 ml	2.08 g

MS-C12-TP	C_{12}TAB	PAA	$NH_3•H_2O$	TPOS
	0.47 g	2.0 g	2.2 ml	2.66 g
MS-C14-TP	C_{14}TAB	PAA	$NH_3•H_2O$	TPOS
	0.51 g	2.0 g	2.2 ml	2.66 g
MS-C16-TP	C_{16}TAB	PAA	$NH_3•H_2O$	TPOS
	0.55 g	2.0 g	2.2 ml	2.66 g
MS-C18-TP	C_{18}TAB	PAA	$NH_3•H_2O$	TPOS
	0.59 g	2.0 g	2.2 ml	2.66 g

3.2 Adsorption of HMSs

In this work, prepared a series of dilute concentrations of Butyl rhodamine B solution. Weigh 10 mg of Butyl rhodamine B solid into a 100 mL volumetric flask and constant volume. Accurately weigh 1 mL, 2 mL, 3 mL, 4 mL, and 5 mL of the solution in a 50 mL volumetric flask and prepare 0.002 mg/mL, 0.004 mg/mL, 0.006 mg/mL, 0.008 mg/mL and 0.01mg/mL through constant volume respectively. Absorbance is measured at the maximum absorbance (558 nm) and the standard curve is drawn. Finally, calculate the standard curve equation of concentration and absorbance. Weigh 0.2 g hierarchical mesoporous silica samples (MS-C16-TE) and mesoporous silica nanoparticle samples (MS-C18-TP) respectively, then 0.2 g of the silica sample was dispersed in 20 mL of Butyl rhodamine B solution with a concentration of 0.01 mg/ml. Put Butyl rhodamine B solution mixed with silica samples in the ultrasound machine quickly to disperse into uniformity, take Butyl rhodamine B solution in 10 min, 40 min, 3 h, 6 h and 9 h to centrifugation, the centrifugal speed is 10,000 rpm. After adsorption and centrifugation, the supernatants of the solution were collected. Initial and final concentrations were determined by a UV absorbance band at 558 nm. The adsorption performance of Butyl rhodamine B is expressed by the decolorization rate of the solution, and the adsorption rate of different structure mesoporous materials (*Pm3n* and *P6mm*) were investigated.

Decolorization rate =（Po-Pt）/Po

Po: The mass concentration of Butyl rhodamine B before adsorption.

Pt: The mass concentration of Butyl rhodamine B after adsorption.

Chapter 4 Results and discussions

4.1 Characterization of hierarchical mesoporous silica

4.1.1 XRD patterns

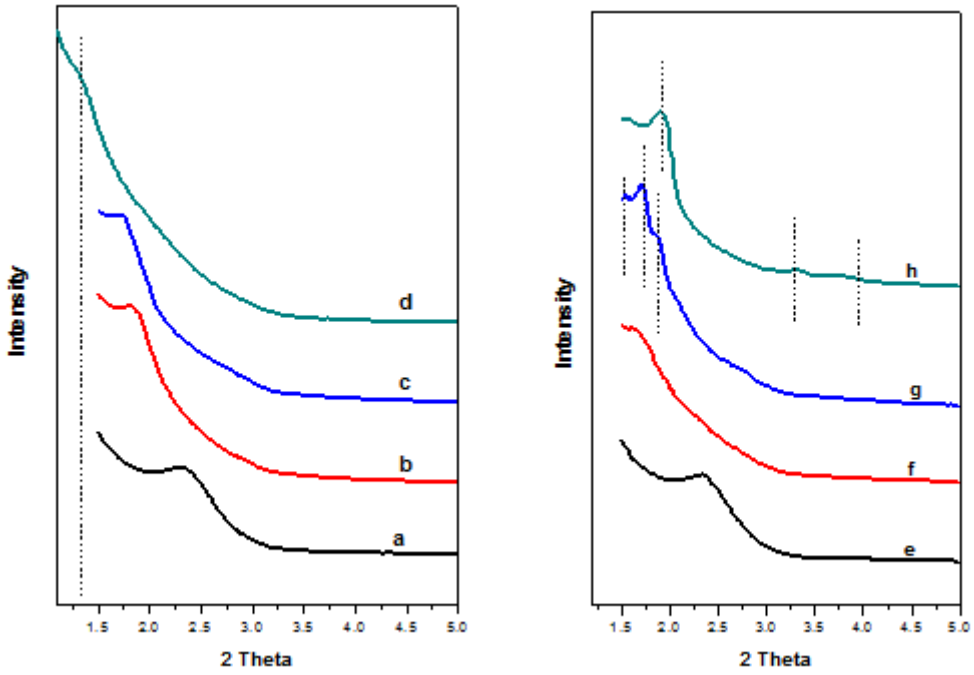

Figure 2. XRD patterns of HMSs synthesized by different templating complexes and silicon precursor. (a) MS-C12-TE, (b) MS-C14-TE, (c) MS-C16-TE, (d) MS-C18-TE; (e) MS-C12-TP, (f) MS-C14-TP (g) MS-C16-TP, (h) MS-C18-TP.

Figure 2 showed the XRD patterns of HMSs synthesized by the different templating complexes and silicon precursor are different. The HMSs synthesized by C_{16}TAB with TEOS or TPOS showed three resolved diffraction peaks which were indexed to (200), (210), and (211) character diffractions of the cubic (*Pm3n*) mesostructure of mesoporous silica, indicating three-dimensional mesoporous were synthesized in this experimental method. By changing the cationic surfactant and silicon precursor in the synthesis process, the morphology and the interior structure of the nanoparticles could be adjusted. When we use C_{18}TAB as polymer-surfactant complex and TPOS as silicon precursors, The XRD patterns exhibited three distinct diffraction peaks, which were indexed to (100), (110) and (200) characteristic diffractions of the cubic p6mm mesostructure symmetry. Highly ordered mesoporous HMS nanoparticles with 2D hexagonal structure (*P6mm*) were firstly obtained in polymer-surfactant synthetic system. It is worth noting that the size of nanoparticles were about 50-100 nm which was obtained from the Fig. 4h. It also can be seen from

Fig. 5 that due to the possible accumulation between particles, the diameter of the particles has reached 100-200 nm, but it still belongs to the category of nanoparticles.

4.1.2 TEM images

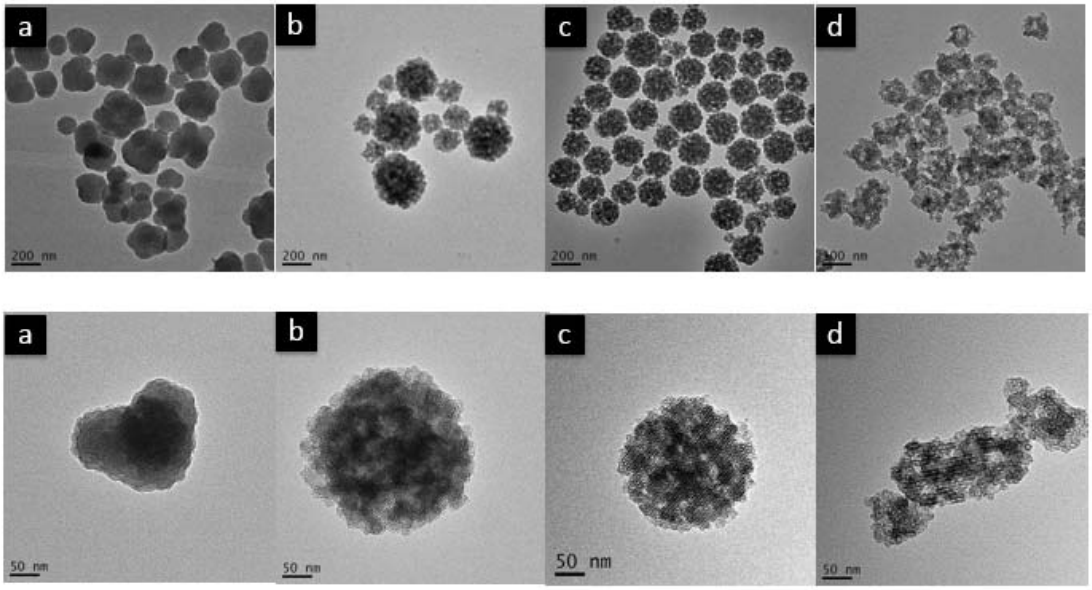

Figure 3. High-resolution TEM images of HMSs synthesized by different templating complexes and the same silicon precursor TEOS. (a) MS-C12-TE, (b) MS-C14-TE, (c) MS-C16-TE, (d) MS-C18-TE.

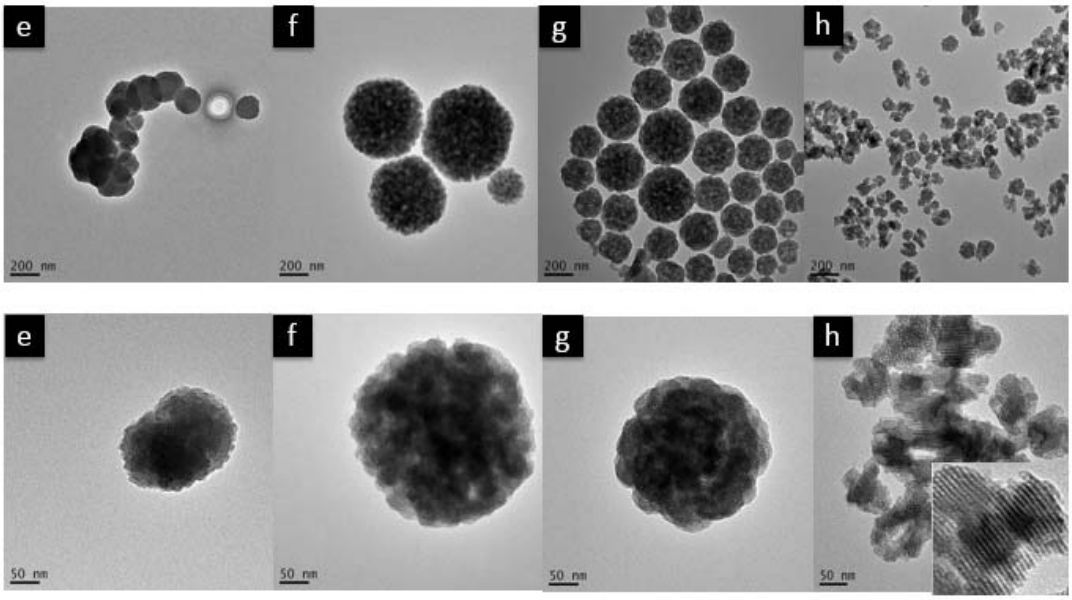

Figure 4. High-resolution TEM images of HMSs synthesized by different templating complexes and the same silicon precursor TPOS. (e) MS-C12-TP, (f) MS-C14-TP (g) MS-C16-TP, (h) MS-C18-TP.

Transmission electron microscopy (TEM) images and dynamic light scattering (DLS) curves (Fig. 5) showed that all the sample were generally submicrometer spherical morphology with a particle size range of 50–300 nm. High-resolution TEM images (Fig. 3a and Fig. 4a) of the microspheres synthesized by C_{12}TAB and TEOS, TPOS showed that there is no hierarchically mesoporous structure just a single microspore structure. The size of the particles reached 300 nm due to the aggregation of particles while the actual single particle size is less than 100 nm. MS-C14-TE and MS-C14-TP exhibited two different kinds of mespores (ordered mesopores and secondary interstitial nanopores) like samples synthesized by C_{16}TAB as polymer-surfactant complex. The generation of the mesopores and the secondary interstitial nanopores was due to the surfactant micelles and the phase-separated PAA, respectively. Furthermore, the alignment of the mesopores kept long-range order within the entire nanoparticle as shown in Fig. 3c and Fig. 4g, indicating that the presence of the secondary interstitial nanopores did not disturb the single-crystal characteristic of the HMSs nanoparticles. High-resolution TEM images revealed that the mesopores of the MS-C18-TP possessed a high degree of periodicity within the whole particle, indicating that the MS-C18-TP exhibited a single-crystal-like feature. It can also be seen from the figure that the nanoparticle pore structure is a two-dimensional hollow straight tube.

4.1.3 DLS curves

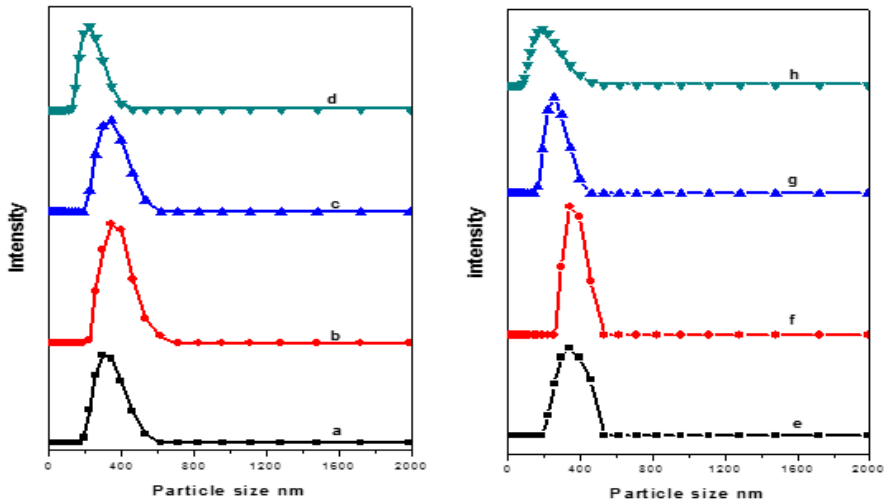

Figure 5. DLS curves of HMSs synthesized by different templating complexes and silicon precursor. (a) MS-C12-TE, (b) MS-C14-TE, (c) MS-C16-TE, (d) MS-C18-TE; (e) MS-C12-TP, (f) MS-C14-TP (g) MS-C16-TP, (h) MS-C18-TP.

From the dynamic light scattering diagram, we can find that the diameter of the sample particles is mostly distributed between 100-500 nm, which can correspond to the TEM image and truly reflect the size of the particles. However, MS-C12-TE and MS-C12-TP have higher particle size distribution due to aggregation between particles, which can also be clearly seen in TEM images, indicating that this type of mesoporous silica materials have poor dispersibility in water.

4.1.4 Nitrogen adsorption-desorption

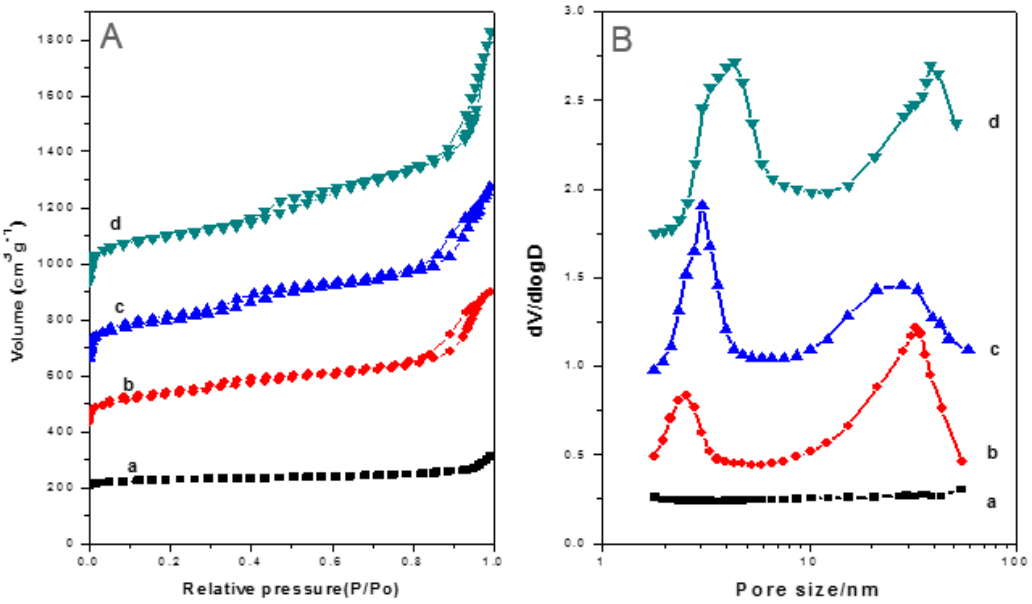

Figure 6. (A) Nitrogen adsorption-desorption isotherms and (B) PSD curves of the calcined HMSs synthesized at different templating complexes. (a) MS-C12-TE, (b) MS-C14-TE, (c) MS-C16-TE, (d) MS-C18-TE.

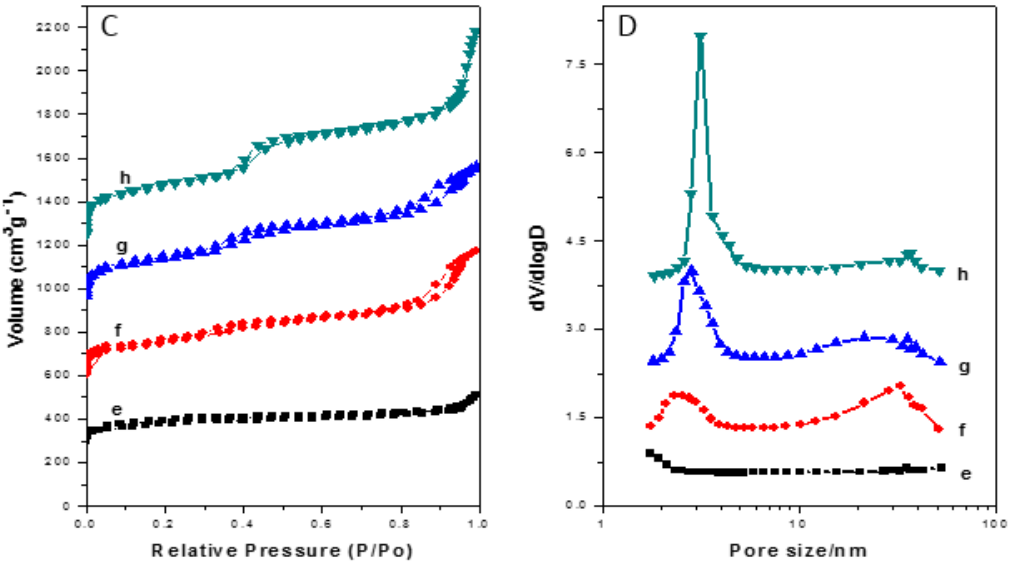

Figure 7. (C) Nitrogen adsorption-desorption isotherms and (D) PSD curves of the calcined samples synthesized at different templating complexes. (e) MS-C12-TP, (f) MS-C14-TP, (g) MS-C16-TP, (h) MS-C18-TP.

Table2. Structural parameters and pore properties of calcined products

Sample	BET surface area /$m^2 \cdot g^{-1}$	Mespore Size /nm	Secondary Nanopore size /nm	Mespore Volume /$cm^3 \cdot g^{-1}$
MS-C12-TE	93	<2	-	0.17
MS-C14-TE	390	2.4	~30	0.73
MS-C16-TE	518	2.6	~30	0.95
MS-C18-TE	591	3.8	~40	1.38
MS-C12-TP	294	<2	-	0.12
MS-C14-TP	531	2.4	~30	0.88
MS-C16-TP	636	2.6	~30	0.92
MS-C18-TP	812	2.8	~30	1.44

The nitrogen adsorption-desorption isotherms and pore size distribution curves of the HMS nanoparticles synthesized by different polymer-surfactant complexes and silicon precursors are shown in Fig. 6 and Fig. 7. For the HMS nanoparticles, MS-C12-TE and MS-C12-TP exhibited type Ⅰ isotherms, and in the pore size distribution curves, we can also found that the pores of sample is smaller than 2 nm, which is micropore typically. The XRD characterization has diffraction peaks at low angles (see Figure 1), which are indicative of an ordered microstructure. And for other HMS nanoparticles synthesized by C_{14}TAB, C_{16}TAB, C_{18}TAB and different silicon precursors (TPOS, TEOS), Nitrogen adsorption desorption characterization curve all exhibited type Ⅳ isotherms with three distinct adsorption steps at the relative pressure of 0.3-0.5, 0.8-0.95, 0.95-0.99, respectively. The first at a relative pressure of 0.3–0.5 correspond to the relatively narrow peaks at about 2-4 nm in the pore size distribution curves, depending on the length of cationic surfactants, which were the cage-like pore size of the mespores of HMS nanoparticles. With the increase of the length of cationic surfactants, the first step of 0.3–0.5 became gradually obvious. This phenomenon is in

accordance with the increase of mespores size about 3 nm shown in pore size distribution curves. The second adsorption step at a relative pressure of 0.8–0.95 gave rise to a broad pore size centered at 20-40 nm corresponding to the secondary interstitial nanopores which was proved by the TEM images Fig. 3 and Fig. 4. The third adsorption step, where relative pressure p/p0 = 0.95–0.99, was due to the voids of the aggregated nanoparticles. The textural parameters such as specific surface area, pore volume and pore size are given in Table 2. As shown in the Table 2, we could conclude that as the alkyl chain of the surfactant complexes increases in the reaction system, the pore size of the synthetic materials continue to increase, specific surface area and pore volume are also increasing. This is because as the alkyl chain of the surfactant in the reaction system increases, the electrical attraction between the positive and negative surfactant ions increases, larger micelles is easily to form, thereby increasing the size of the pore.[19,27]

4.2 Adsorption of HMSs

4.2.1 Drawing of standard curve

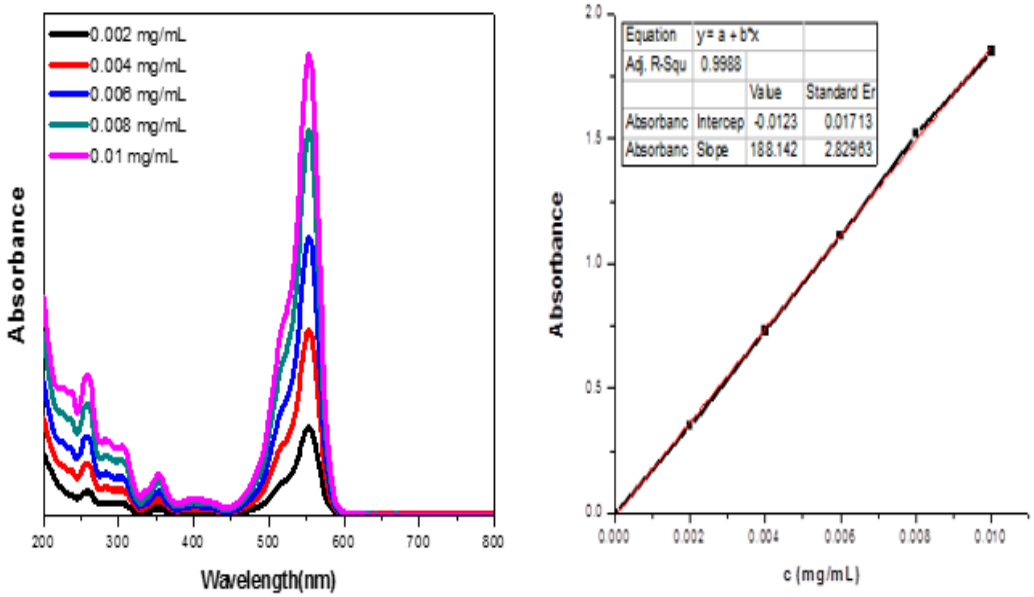

Figure 7. UV-vis Spectrophotometer of different concentration of Butyl rhodamine B solution and standard curve of Butyl rhodamine B.

4.2.2 Adsorption of Butyl rhodamine B

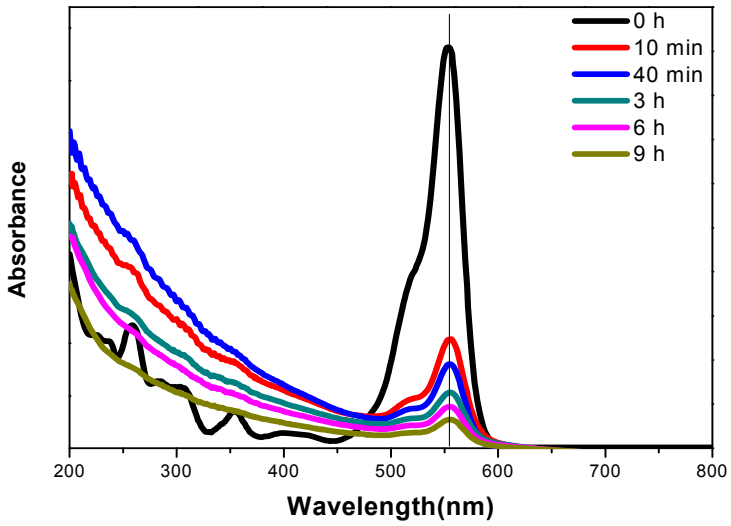

Figure 8. UV-vis Spectrophotometer of Butyl rhodamine B solution adsorbed by MS-C16-TE samples.

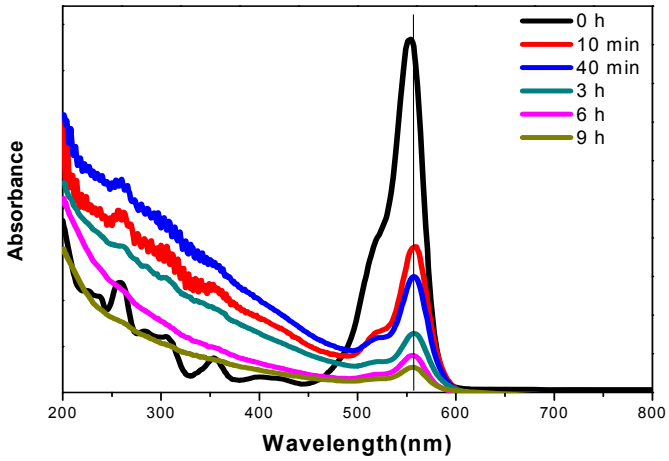

Figure 9. UV-vis Spectrophotometer of Butyl rhodamine B solution adsorbed by MS-C18-TP samples.

Figure 10. Photos of Butyl rhodamine B solution adsorbed by HMSs. A. MS-C16-TE, B. MS-C18-TP.

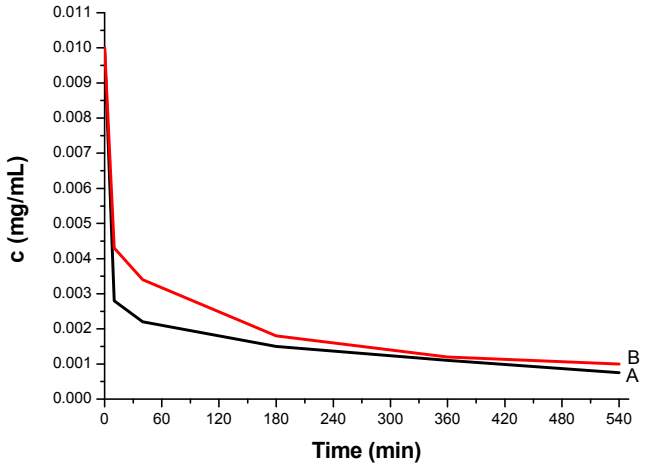

Figure 11. Adsorption rate of Butyl rhodamine B solution adsorbed by different samples. A. MS-C16-TE, B. MS-C18-TP.

From Fig. 7, we can know that the absorbance of Butyl rhodamine B solution is linearly proportional to the concentration of the solution, and the value of absorbance increases as the solution concentration increases. From the Figure 10. The color of the s Butyl rhodamine B solution gradually faded over time, indicating that this material is constantly adsorbing Butyl rhodamine B, resulting in a decrease in the concentration of the solution. As shown in the Figure 11, we can see that the Butyl rhodamine B adsorbed by MS-C16-TE with hierarchically porous structure is very fast, which can reach the two thirds of amount of all Butyl Rhodamine B after 10 minutes, after that, the adsorption rate become flat, after 9 hours, decolorization rate reached 92.5%. The adsorption of MS-C18-TP nanoparticles is less than MS-C16-TE, decolorization rate reached 90% after 9 hours, which is slightly lower than the decolorization rate of Butyl rhodamine B absorbed by MS-C16-TE. Overall, compared with MS-C18-TP (*P6mm*) nanoparticles, hierarchical MS-C16-TE (*Pm3n*) materials showed faster adsorption rate. MS-C16-TE (HMSs) are synthetic silicate materials that have different size of mesopores, comparatively large surface areas and longer hole channel, which lead to higher adsorption rate. Although MS-C18-TP (MSNs) have uniform mesopores, high specific surface area and highly ordered mesoporous, the adsorption rate of two-dimensional hexagon hexagonal structure (*P6mm*) is slower than three-dimensional cubic (*Pm3n*) mesostructure.

Chapter 5 Conclusions

In summary, a series of hierarchically mesoporous silica nanoparticles were synthesized by different templating complexes and silicon precursor, they exhibited different mesoscopic structures. When we used C_{12}TAB with TEOS or TPOS as the silicon precursor, we synthesized single crystal microporous silica materials. When we used Cetyltrimethylammonium bromide as a templating agent, we successfully synthesized a three-dimensional structure (*Pm3n*) hierarchical mesoporous silica material, which exhibited large specific surface area and pores volume, and in the adsorption test of Butyl rhodamine B, it showed a very fast adsorption rate, which will have important applications in adsorption and separation, functional materials. And ordered mesoporous nanoparticles (MSNs) with 2D hexagonal structure (*P6mm*) were firstly obtained in polymer-surfactant synthetic system (C_{18}TAB+TPOS). Notably, this kind of material exhibited remarkably large surface area (812 $m^2 \cdot g^{-1}$) and pore volume (1.44 $cm^3 \cdot g^{-1}$) with the size of range of 50-100 nm which has broad application prospect in different field, such as sewage treatment, nanomedicine and functional materials. Finally we also found that the hierarchical structures were mainly based on the length of cationic surfactants, as the alkyl chain grows, the pore size and specific surface area of mesopores also increase. This method of using a complex as a template will have potential application value for the preparation of other hierarchical mesoporous silica and mesoporous silica nanoparticles.

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